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Structural Properties of Organic Chemicals as Predictors of Biodegradation and Microbial Toxicity in Soils

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STRUCTURAL PROPERTIES OF ORGANIC CHEMICALS AS PREDICTORS OF BIODEGRADATION AND MICROBIAL TOXICITY IN SOILS

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ABSTRACT

The evaluation of a chemical's persistence in soil is a major source of uncertainty in environmental risk assessments. Structure-activity relationships (SARs) may provide a useful estimation tool for biodegradability and toxicity of chemicals in soils; however, experiments must be designed to minimize or account for competing loss processes. Biodegradation and toxicity SARs have been described for groups of structurally related molecules in soils, but multiple SARs will undoubtedly be required to estimate properties from large data sets that include dissimilar compounds. These studies provide evidence that the SAR approach has applicability to environmental risk assessments for chemicals in soils, despite important limitations to our ability to extrapolate SARs from one homologous series of chemicals to another.

INTRODUCTION

Prediction of chemical persistence in soils is an essential component of environmental risk assessments, yet rigorous, quantitative methods are lacking to make these estimates. Howard

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et al. [1] pointed out that development of structure/biodegradability relations (SBR) is hindered by the lack of consistent, quality controlled data. That is, there is a general lack of uniformity among researchers in selection of endpoints to express degradability; and there is poor reproducibility of data for those tests used. Until the quality of data are ensured and uniform tests implemented, SARs are not likely to be developed from large data sets.

Even greater obstacles than those mentioned above may thwart the use of SARs in soil systems; namely, the inherent complexity and heterogeneity of soils may mask existing SARs even for simple experiments designed to measure single endpoints. However, based on results from our own experiments and those of others, we propose that the drawbacks to development of SARs for soil data are surmountable, primarily by designing experiments to account for multiple processes that occur simultaneously and by not extrapolating beyond the range of chemical structures for which a given SAR is valid.

FACTORS INFLUENCING ENVIRONMENTAL PROCESSES IN SOILS

Many physical, chemical, and biological properties of soils act in concert to determine the fate of a chemical contaminant. These include soil pH, temperature, percent base saturation, cation ion exchange capacity, nutrient status, organic carbon content, presence of other contaminants, and previous exposure history. Not only are these properties subject to quotidian and seasonal changes, they also vary horizontally and vertically in the soil matrix. Disappearance of a contaminant from soil can occur not only by biological transformation and/or mineralization (typically to carbon dioxide and water), but also by volatilization, oxidation, hydrolysis, reduction, partitioning into organic carbon, and interaction with clay minerals. In natural systems, leaching, binding to dissolved organic matter, association with microparticulates in solution, and uptake by plants and animals may also effect chemical dissipation. Within the microbial community, huge fluctuations in numbers and species can occur within brief time periods to further complicate experimental measurements of chemical fate and effects.

SARs FOR CHEMICALS IN SOILS

SARs have been successfully used to describe the sorption of non-ionized, organic chemical contaminants in soils [2]. Organic

carbon content of the soil is the single most important factor for predicting retention on soil [3] and can be expressed as a chemical-specific or as a chemical- and soil-specific parameter (K_{OC} and K_p, respectively). Both parameters can be estimated from the octanol:-water partition coefficient (K_{OW}) of a substance [3]

The utility of SARs in sorption studies is due partly to the fact that sorption behavior is governed largely by the single process of partitioning [4] and other processes that can interfere with the K_{OW}-sorption correlation are minimized by standard experimental procedures [5]. For example, sorption measurements based on batch extractions are carried out in saturated soils, where the opportunity for aerobic microbial degradation is nearly eliminated. Furthermore, volatilization losses are minimized by using either stoppered flasks or zero headspace extractors [5, 6].

Even though volatilization, biodegradation, and leaching may be important loss processes under natural conditions and these processes are not accounted for in sorption measurements using batch extractions, chemical retention in soil has been accurately estimated by using K_{OW} values to calculate sorption. The broad applicability of these sorption SARs for modelling the behavior of organic chemicals in soils is illustrated by Leistra [7] and Mackay, et al. [8].

TOXICITY OF CHEMICALS TO SOIL MICROORGANISMS

Only a few studies have been conducted to explore the influence of chemical structure on toxicity and degradability of organic compounds in soils. Those studies where physicochemical properties correlated well with toxicity were conducted for structurally similar molecules. For example, Walton, et al. [9] evaluated the effects of 19 hazardous organic chemicals on microbial respiration in two slightly acidic soils from the Southeastern United States. SAR analyses for the entire group, which consisted of acrylonitrile, furan, methyl ethyl ketone, tetrahydrofuran, benzene, toluene, 1,2-dichloroethane, p-xylene, chlorobenzene, chloroform, nitrobenzene, trans-1,4-dichloro-2-butene, cis-1,4-dichloro-2-butene, 1,2-dichlorobenzene, 1,2,3-trichloropropane, carbon tetrachloride, 1,2-dibromoethane (ethylene dibromide), 1,2,4,5-tetrachlorobenzene, and hexachlorobenzene failed to show correlations of effects on soil microbial respiration with $\log_{10} K_{OW}$, water solubility, vapor pressure, Henry's law constant, or rat acute toxicity. However, analysis of a subset of chemicals relatively similar in structure (i.e.,

benzene, toluene, p-xylene, chlorobenzene, dichlorobenzene, tetrachlorobenzene, and hexachlorobenzene) yielded good correlations of respiratory effects with $\log_{10} K_{ow}$ for the Captina silt loam soil that could be described by the following equation:

$$y = 0.239 - 0.064x, \quad N = 7, \quad r = 0.91 \qquad (1)$$

where y is $\log_{10}$ [(CO_2 $EFFLUX_{treatment}$)/(CO_2 $EFFLUX_{control}$)], x is $\log_{10} K_{ow}$, N is the number of chemicals, and r is the correlation coefficient and is the proportion of explained variation. This correlation was slightly improved by using molecular connectivity ($^1\chi$) instead of $\log_{10} K_{ow}$:

$$y = 0.456 - 0.114x, \quad N = 7, \quad r = 0.94 \qquad (2)$$

where x is $^1\chi$. Correlations were not as good for the McLaurin sandy loam soil, which may have been due to the lower organic carbon content of the McLaurin sandy loam (0.66%) compared with the Captina silt loam (1.49%). In studies of pentachlorophenol and mercuric chloride ($HgCl_2$) in a variety of soil types, Zelles et al. [10] concluded that organic matter was an important modifier of microbial endpoints.

Despite the inability to correlate chemical effects on soil microbial respiration with physicochemical properties of all 19 test chemicals, structure-activity analysis of sorption data showed an excellent linear correlation (r = 0.94) between experimentally determined K_{oc} and K_{oc} predicted from K_{ow} [6]. Because K_{oc} experiments were conducted with a mixture of chemicals, this finding indicates that predictive equations for sorption of individual hydrophobic organics in sediments can be applied with high reliability to mixtures of volatile and semivolatile organics in soils.

Many types of chemicals have been tested for adverse effects on soil microbial communities without yielding SARs, perhaps because the test chemicals have been structurally too diverse for a single SAR to apply. For example, 29 pesticides were tested by Bartha, et al. [11] for their influence on nitrification and CO_2 production by soil microorganisms. The pesticides were structurally heterogeneous and included carbamates, thiolcarbamates, cyclodienes, phenylureas, organophosphates, anilides, amides, and

triazines. The authors related molecular structure to persistence and effects in soil for groups of chemicals; however, no SAR emerged that was collectively applicable to the pesticides.

Zelles et al. [12] used ATP content, respiration, and fluorescein diacetate hydrolysis as measures of effects on soil microorganisms for atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine), pentachlorophenol, 4-chloroaniline, chloroacetamide, 4-nitrophenol, mercuric chloride ($HgCl_2$), zineb (zinc ethylene-1,2-bis-dithiocarbamate), captan (N-trichloromethylmercapto-4-cyclo-hexene-1,2-dicarboximide), lindane (γ-1,2,3,4,5,6-hexachlorocyclohexane), and 4-nitrophenol. The results were very useful as chemical-specific observations of toxicity to soil microorganisms; however, no predictive SAR was apparent for this collection of structurally dissimilar compounds.

DEGRADABILITY OF CHEMICALS IN SOILS

In analyses of the influence of chemical structure on microbial degradation, Alexander and co-workers formulated guidelines for the influence of chemical substitution on decomposition of phenoxyalkyl carboxylic acid herbicides and related compounds [13] and of substituted benzenes [14]. Bossert and Bartha [15] found that biodegradation in soil of 10 polycyclic aromatic hydrocarbons, which ranged from three to five rings in size, correlated positively with water solubilities of the compounds. These examples provide evidence that predictive SBR can be developed from soil experiments when the range of chemical structures permits a systematic structure-activity evaluation.

Control of nonbiological chemical losses in soils is necessary in experiments to measure biodegradation rates for chemical contaminants; however, the commonly used methods to inactivate microorganisms (i.e., mercuric chloride, sodium azide, propylene oxide, autoclaving, and gamma irradiation) are either not effective sterilants or alter soil properties [16-18].

Cantier et al. [19] compared degradation of propyzamide and nine analogues in sterile and nonsterile soils to establish a relationship between degradation rate constants and physicochemical parameters. The results indicated that chemical degradation was the primary mechanism for loss of propyzamide and its analogues; however, microbial degradation could not be excluded because transformation occurred more rapidly in a nonsterilized soil than in

sterilized soil. Bossert and Bartha [15] and Walton et al. [6] found that abiotic losses may have obscured or interfered with structure-biodegradability relations for volatile organics.

CONCLUSION

Structure-activity relationships have been developed for biodegradation and toxicity of organic contaminants in soils; however, nonbiological loss processes, such as volatilization, oxidation, hydrolysis, and reduction, must be controlled or accounted for in experiments to develop biological SAR data. Results of experimental studies indicate that SARs for biodegradation and toxicity cannot be extrapolated beyond the classes of chemicals for which the data were obtained. Despite these limitations, SARs have the potential to be useful estimation tools for environmental risk assessments of contaminant behavior in soils.

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